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TITLE: THE ISOTOPIC ANALYSIS OF DIMETHYL SELENIDE

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THE ISOTOPIC ANALYSIS OF DIMETHYL SELENIDE

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ABSTRACT

The separated isotopes of selenium may be used as stable precursors for the synthesis of radio-bromine isotopes for positron emitter tomographic diagnostics. As part of a project to find a suitable distillation method for separating selenium isotopes, the need arose to study the organo-metallic compound dimethyl selenide. The complexity of the mass spectrum tended to obscure the isotope effect with 35 major peaks being measured. A least-squares fitting procedure was developed for the 13 fragmentation factors as well as a few hundredths of a percent, yet no sizeable separation was observed across the test column. According to these measurements, the effect of one mass unit increase in the selenium ictope results in less than 10 ppm in the vapor pressure of the compound.

DISCLAIMER

The separated isotopes of selenium may be used as stable precursors for the synthesis of radio-bromine isotopes for positron emitter tomographic diagnostics. We have been engaged in a project to search for a suitable distillation method for separating the selenium isotopes. This report is of the studies made on dimethyl selenide as a distilling medium.

A small laboratory test column was used for the purpose which was 93 cm long, with an inside diameter of 1.4 cm which was packed with Helipak #3015 (Podbelniak, Inc.). The column subtended four equally spaced sampling leaks which fed directly to the mass spectrometer about 15 m away. Each column section contained an estimated 30 theoretical plates. The column was studied at a reduced pressure of 130 torr corresponding to a column temperature of 10°C. All processing equipment for the selenium compound was housed in a glovebox, due to its extreme toxicity.

The mass spectrum obtained from one of these leaks is shown in Fig. 1. Thirty-five peaks are involved, discounting a few small peaks which were ignored. Some assignments are shown in the figure, but a considerable redundancy is present at most mass peaks, with up to four contributions to each peak.

The selenium stable isotopes are of mass:

$$m_k = 74,\ 76,\ 77,\ 78,\ 80 \text{ and } 82$$

Observed fragment types are

$$Se^+,\ SeH^+,\ SeH_2^+,\ SeH_3^+$$
$$SeCH^+,\ SeCH_2^+,\ SeCH_3^+,\ SeCH_4^+$$
$$SeC_2H_3^+,\ SeC_2H_4^+,\ SeC_2H_5^+ \text{ and } SeC_2H_6^+$$

The total mass of an ion, m''_i, comes from an isotope of mass m_k and a fragment of mass m'_j where:

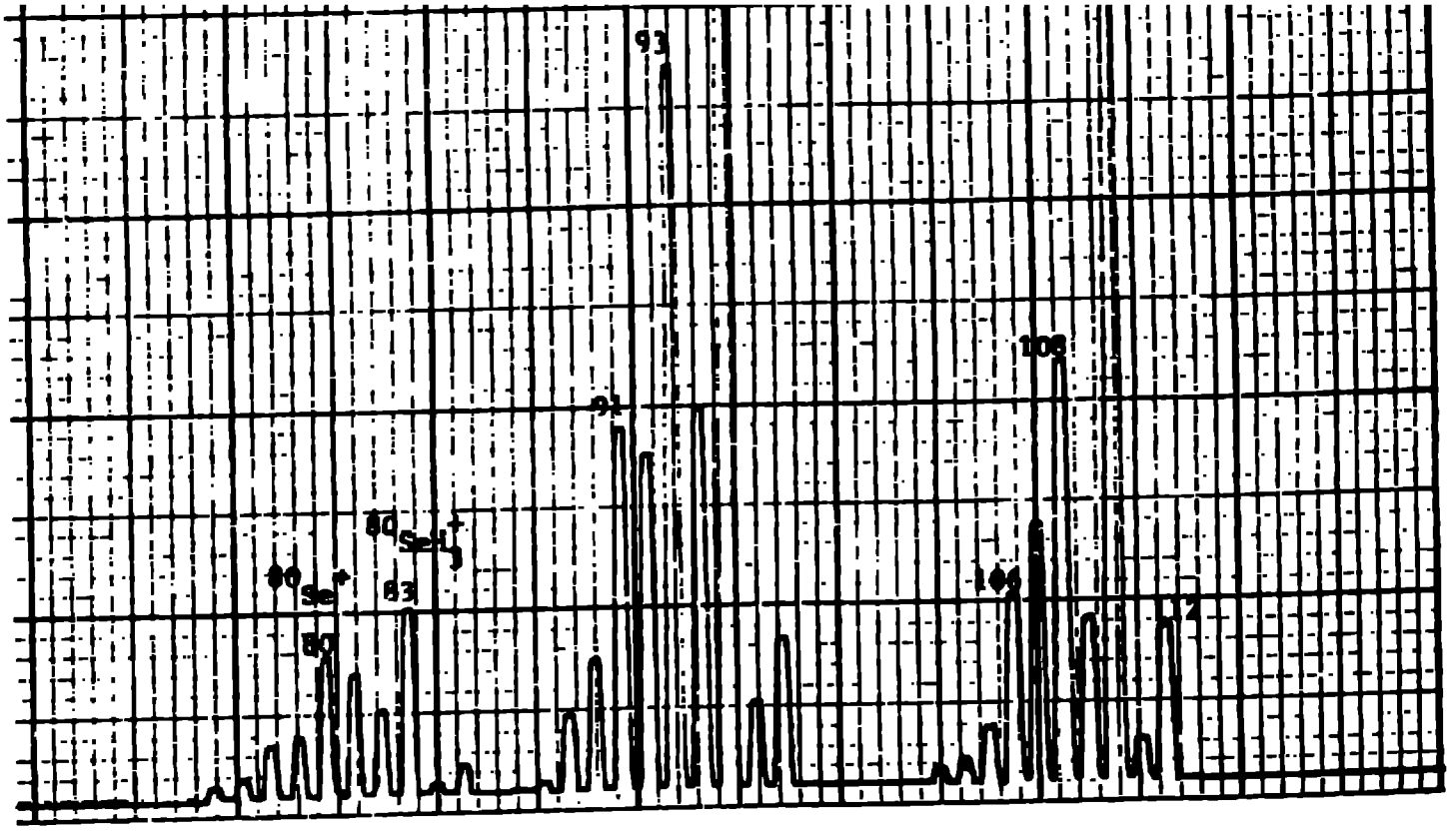
$$m'_j = 0,\ 1,\ 2,\ 3,\ 12,\ 13,\ 14,\ 15,\ 16,\ 27,\ 28,\ 29 \text{ and } 30$$

and where

$$m''_i = m_k + m'_j \qquad (1)$$

The resulting values of m''_i range from mass 74 to 112.

Apart from the selenium isotopic variations there are small contributions from the minor isotopes of carbon and hydrogen to this spectrum. For our purposes, the hydrogen isotope contributions were neglected but the carbon-13


93
91
$^{80}Se^{+}$
$^{80}SeH_3^{+}$
83
80
104
106

sophisticated procedure could have been developed to take account of the carbon isotope contribution.

At this point then, the theoretical or predictive function for interpreting the spectrum consists of six parameters, c_k, which are the atom fractions of the selenium isotopes, and thirteen parameters, f_j, which are the fragmentation factors. The contribution of a particular fragment of mass m_j' and from isotope of mass m_k is of amount $f_j c_k$ to the ith spectral peak where m_i' is the sum of such terms, or

$$T_i = \Sigma_{jk}\, f_j c_k \qquad (2)$$

The deviation of this predicted value from the observed height, P_i, is $P_i - T_i$ and the function to be minimized in a least-squares fitting is

$$S = \tfrac{1}{2}\, \Sigma_i\, (P_i - T_i)^2 \qquad (3)$$

To satisfy this minimzation process for the parameters, f_j, we wish to cause the various functions to vanish given by

$$\partial S/\partial f_j = 0 \qquad (4)$$

Each of these functions is a linear function of the f's (though not of the c's), and may be written in matrix notation

$$Wf = V \qquad (5)$$

where the elements of W are bilinear combinations of the c's of the form $\Sigma c_k c_l$ and the elements of V are of the form $\Sigma c_k P_i$. Thus, if one knows (or assumes) the c's, the f's are found from eq. 5 as

$$f = W^{-1}V \qquad (6)$$

The procedure for solution of the c's is somewhat similar, but is complicated by the constraint of $\Sigma c_k = 1$ so that the c's are not independent. In this case, Eq. 4 does not hold, but rather

$$\partial S/\partial c_k = \lambda \qquad (7)$$

where λ is an undetermined constant. We may form the matrices W, V, and c as before with f's replacing the c's of the previous description, but their relationship is

$$Wc - V = \lambda I \qquad (8)$$

where I is a column vector of unit elements. From Eq. 8 we have

$$c = D + \lambda E \qquad (9)$$

where

$$D = W^{-1}V \qquad (10)$$

$$E = W^{-1}I \qquad (11)$$

Then $\Sigma c_k = 1$ implies

$$\lambda = (1-\Sigma D_k)/\Sigma E_k \qquad (12)$$

and the elements of a c are given by Eq. 9.

This method of analyzing a sample of dimethyl selenide starts with an assumption of one of the vectors c or f, then calculates the other, permitting the first to be recalculated etc. Thus it is strictly speaking an iterative method and is open to questions of convergence. In this example, however, the f's and c's converged very rapidly for a given spectrum. Figure 2 shows a printout of a fitted mass spectrum.

Having obtained an interpretation for each spectrum, we next were faced with interpreting the resulting isotopic analyses from points along a test distillation column in order to evaluate the relative separation factors or vapor pressures of the several isotopes. Since it was evident from preliminary evidence that these effects were very small in our test column, it is appropriate to consider a linear perturbation upon a uniform column. If the atomic weight of selenium is taken to be

$$M = \Sigma c_i^o m_i \qquad (13)$$

where c_i^o is the normal abundance of the ith isotope, then the variation along the column is given by

$$c_i(n) = x_i + \varepsilon n(m_i - M) \qquad (14)$$

where n is the number of theoretical plates along the column and is assumed to be known. The parameters to be fitted are x_i (i=1...6) and ε. This linear least-squares ftting problem is straightforward except that, as before, the set x_i are not independent but instead satisfy $\Sigma x_i = 1$.

Figures 3 and 4 are a printout of the best fitted results to a full column survey on two different days. On Oct. 24, the sequence was #4 (top) to #1 (Bottom), while on Oct. 27 this was reversed. Although each set of data confirms a small vapor pressure effect, the predicted result of such an effect is so small as to lend doubt that this result is real.

Thus the conclusion from this study is that the isotopic vapor pressure effect in dimethyl selenium is either very small (about 10 ppm) or zero.

ITERATE

Mass	Observed	Calculated	Difference
76	0.388	0.399	0.011
77	0.492	0.478	-0.014
78	1.267	1.280	0.013
79	1.013	1.014	0.001
80	2.919	2.913	-0.007
81	1.989	1.989	0.000
82	1.517	1.519	0.002
83	2.637	2.639	0.002
84	0.216	0.208	-0.008
85	0.451	0.447	-0.004
87	0.129	0.117	-0.012
88	0.258	0.276	0.018
89	1.620	1.663	0.043
90	2.553	2.580	0.027
91	6.619	6.603	-0.016
92	5.723	5.699	-0.024
93	13.174	13.169	-0.006
94	6.501	6.509	0.007
95	14.281	14.288	0.006
96	1.399	1.400	0.001
97	2.334	2.340	0.006
103	0.261	0.223	-0.038
104	0.412	0.373	-0.040
105	0.989	0.864	-0.024
106	2.704	2.687	-0.017
107	3.668	3.690	0.022
108	5.977	5.996	0.020
109	2.162	2.170	0.008
110	12.563	12.554	-0.009
111	0.417	0.357	-0.060
112	2.252	2.251	-0.001

Isotope Abundance		Fragmentation Factors		
Se- 74	0.935	F(0)	4.031	Se^+
Se- 76	9.422	F(1)	1.636	HSe^+
Se- 77	6.998	F(2)	2.302	
Se- 78	23.530	F(3)	4.963	
Se- 80	50.198	F(12)	1.831	CSe^+
Se- 82	9.017	F(13)	15.990	
		F(14)	12.371	
		F(15)	25.950	CH_3Se^+
		F(16)	0.567	
		F(27)	2.014	$C_2H_3Se^+$
		F(28)	0.246	
		F(29)	3.981	
		F(30)	24.064	$(CH_3)_2Se^+$

S.D. 0.001146

Figure 2 - The Least-squares fitted spectrum

Epsilon= .000010

	Intercept	Ybar
Se-74	.817	.819
Se-76	9.428	9.441
Se-77	6.933	6.940
Se-78	23.532	23.543
Se-80	50.265	50.244
Se-82	9.025	9.013

POINT # 4

	CALC.	OBS.	DIFF.
Se-74	.817	.832	-0.015
Se-76	9.428	9.419	0.009
Se-77	6.933	7.014	-0.081
Se-78	23.532	23.529	0.003
Se-80	50.265	50.194	0.071
Se-82	9.025	9.011	0.014

POINT # 3

	CALC.	OBS.	DIFF.
Se-74	.816	.822	-0.006
Se-76	9.419	9.443	-0.023
Se-77	6.929	6.941	-0.013
Se-78	23.524	23.541	-0.017
Se-80	50.279	50.240	0.038
Se-82	9.033	9.015	0.019

POINT # 2

	CALC.	OBS.	DIFF.
Se-74	.815	.813	0.002
Se-76	9.411	9.455	-0.044
Se-77	6.924	6.899	0.025
Se-78	23.516	23.557	-0.041
Se-80	50.293	50.265	0.027
Se-82	9.041	9.010	0.031

POINT # 1

	CALC.	OBS.	DIFF.
Se-74	.813	.809	0.004
Se-76	9.402	9.448	-0.046
Se-77	6.920	6.904	0.016
Se-78	23.509	23.547	-0.038
Se-80	50.307	50.276	0.031
Se-82	9.050	9.017	0.033

Figure 3 - Analysis of the column profile on Oct. 24. Each "observed" spectrum is the mean of three independent scans. The entire set of data has been least-squares fitted to the assumed epsilon and the indicated intercepts. Thirty plates are assumed between points.

Epsilon= .000006

	Intercept	Ybar
Se-74	.811	.813
Se-76	9.438	9.446
Se-77	6.912	6.915
Se-78	23.541	23.547
Se-80	50.276	50.264
Se-82	9.023	9.016

POINT # 4

	CALC.	OBS.	DIFF.
Se-74	.811	.830	-0.019
Se-76	9.438	9.408	0.030
Se-77	6.912	6.987	-0.075
Se-78	23.541	23.526	0.015
Se-80	50.276	50.229	0.047
Se-82	9.023	9.020	0.003

POINT # 3

	CALC.	OBS.	DIFF.
Se-74	.811	.801	0.010
Se-76	9.433	9.470	-0.037
Se-77	6.909	6.886	0.023
Se-78	23.537	23.556	-0.019
Se-80	50.283	50.266	0.017
Se-82	9.027	9.021	0.006

POINT # 2

	CALC.	OBS.	DIFF.
Se-74	.810	.812	-0.002
Se-76	9.428	9.459	-0.031
Se-77	6.907	6.892	0.015
Se-78	23.532	23.563	-0.031
Se-80	50.291	50.267	0.024
Se-82	9.032	9.008	0.024

POINT # 1

	CALC.	OBS.	DIFF.
Se-74	.809	.807	0.002
Se-76	9.424	9.445	-0.021
Se-77	6.905	6.897	0.008
Se-78	23.528	23.545	-0.017
Se-80	50.299	50.294	0.005
Se-82	9.036	9.014	0.022

Figure 4- Similar to Fig.3 but for a different day.